

Amendments to Specification

Please amend the title to read:

--Method of depositing optical quality silica films by PECVD while controlling gas pressure--

Please replace the paragraph commencing at line 26, page 8, with a new paragraph as follows:

-- The ~~High~~^{high} temperature thermal treatments also have their own shortcomings. Optical quality silica films typically require a post-deposition thermal treatment at a high temperature as high as 1350°C in order to eliminate residual optical absorption peaks in the 1.30 to 1.55 μm optical region. --

Please replace the paragraph commencing at line 12, page 10, with a new paragraph as follows:

-- Typically the deposition is carried out with SiH₄ as a raw material gas, N₂O as an oxidation gas is, and N₂ as a carrier gas, although other materials can be used.--

Please replace the paragraph commencing at line 25, page 10, with a new paragraph as follows:

-- The novel PECVD approach in accordance with the invention can provide undoped (no B and/or P) silica films from the oxidation of silane, SiH₄, using nitrous oxide, N₂O. ~~It will then focus on the effect of additional nitrogen, N₂, reactant gas.~~ --

Please cancel the paragraph commencing at line 1, page 11, with as follows:

~~-- This discussion will not consider means of adding ammonia, NH₃, fluorine, F, phosphorus, P, boron, B, or other compounds or elements as a way to control refractive indexes.~~

Please replace the paragraph commencing at line 14, page 14, with a new paragraph as follows:

-- Figure ((4))³ lists the possible chemical reactions (i.e. thermal decomposition reactions) that may result from the exposure of the thirty-five (35) potential as-

deposited compounds to nitrogen at very high temperature. Again, the thermal decomposition reactions (producing a potential post-treatment compound after the high temperature thermal treatment which is different than the potential as-deposited compound before high temperature thermal treatment) have to preserve the need to accommodate the chemical bonds of their constituting atoms. These various reactions present a very clear overview of the limitations of these high temperature thermal treatments:--

Please replace the paragraph commencing at line 14, page 14, with a new paragraph as follows:

-- Figure ((5))4 lists some FTIR fundamental infrared absorption peaks and their corresponding higher harmonics peaks associated with the six (6) residual potential post-treatment compounds that result from thermal decomposition during a high temperature thermal treatment of these silica films in a nitrogen ambient. It is clear from Figure ((5))4 that the higher harmonics of the absorption peaks corresponding to these six (6) residual potential post-treatment compounds contribute to the optical absorption in the 1.30 to 1.55 μm optical bands. The six peaks are: the second vibration harmonics of the HO-H oscillators in trapped water vapour in the micro-pores of the silica films (3550 to 3750 cm^{-1}), which increase the optical absorption near 1.333 to $1.408 \mu\text{m}$; the second vibration harmonics of the SiO-H oscillators in the silica films (3470 to 3550 cm^{-1}), which increase the optical absorption near 1.408 to $1.441 \mu\text{m}$; the second vibration harmonics of the Si:N-H oscillators in the silica films (3300 to 3460 cm^{-1}), which increase the optical absorption near 1.445 to $1.515 \mu\text{m}$; the second vibration harmonics of the SiN-H oscillators in the silica films (3380 to 3460 cm^{-1}), which increase the optical absorption near 1.445 to $1.479 \mu\text{m}$; the third vibration harmonics of the Si-H oscillators in the silica films (2210 to 2310 cm^{-1}), which increase the optical absorption near 1.443 to $1.505 \mu\text{m}$; the fourth vibration harmonics of the Si=O oscillators in the silica films (1800 to 1950 cm^{-1}), which increase the optical absorption near 1.282 to $1.389 \mu\text{m}$; and the fifth vibration harmonics of the N=N oscillators in the silica films (1530 to 1580 cm^{-1}), which increase the optical absorption near 1.266 to $1.307 \mu\text{m}$. --

Please replace the paragraph commencing at line 25, page 18, with a new paragraph as follows:

-- The lack of incorporation of oxygen atoms into the deposition reaction produces, at a microscopic scale, a mixture of the thirty-five (35) undesirable Si-O_x-H_y-N_z potential as-deposited compounds (listed in Figure ((3))2) difficult to eliminate with temperature treatments. --

Please replace the paragraph commencing at line 11, page 19, with a new paragraph as follows:

-- Figure ((6a))5a shows the basic FTIR spectra of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. It is clear that the higher the thermal decomposition temperature of the high temperature thermal treatment in a nitrogen ambient, the better the thermal decomposition of silica films, the better the elimination of: nitrogen, N₂, hydrogen, H₂, and ammonia, NH₃. (i.e. as per the chemical reactions of Figure ((4))3) and the better the FTIR spectra of the treated silica films (i.e. the better the four basic optical absorption peaks): --

Please replace the paragraph commencing at line 12, page 20, with a new paragraph as follows:

-- Figure ((7))6a shows the in-depth FTIR spectra from 810 to 1000 cm⁻¹ of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. This region of the FTIR spectra should show a net separation between the Si-O-Si "in-phase-stretching mode" absorption peak (1080 cm⁻¹) and the Si-O-Si "bending mode" absorption peak (810 cm⁻¹) and should show a deep valley between 850 and 1000 cm⁻¹. It is clear that the higher the thermal decomposition temperature of the high temperature thermal treatment in a nitrogen ambient, the better the separation and the deeper the valley. The reduction and gradual elimination of the Si-OH oscillators, centered at 885 cm⁻¹ (i.e. of some configurations of the SiOH₂ residual

potential post-treatment compounds) using various chemical reactions of Figure ((4))3 is demonstrated to occur following the 600°C thermal treatment in a nitrogen ambient. A residual peak is observed at 950 cm⁻¹, indicating the presence of residual oscillators as a result of the various thermal decomposition reactions of Figure ((4))3. These residual oscillators are associated to the Si-ON oscillators of two (2) of the six (6) residual potential post-treatment compounds: SiONH and SiON₂. It is clear that the higher the temperature of the high temperature thermal treatment from 600 to 1100°C in a nitrogen ambient, the more nitrogen incorporation and the more evident the Si-ON oscillators (i.e. some configurations of the residual potential: SiONH and/or SiON₂ post-treatment compounds). --

Please replace the paragraph commencing at line 5, page 21, with a new paragraph as follows:

Figure ((8a))7a shows the in-depth FTIR spectra from 1500 to 1600 cm⁻¹ of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. This region of interest focuses on the N=N oscillators, centered at 1555 cm⁻¹, of the various post-treatment compounds described by the various chemical reactions of Figure ((4))3. It is apparent that the higher the thermal decomposition temperature of the high temperature thermal treatment in a nitrogen ambient, the better the elimination of N=N oscillators (which fifth harmonics could cause an optical absorption between 1.266 and 1.307 μm) with a complete elimination of residual N=N oscillators (i.e. some configurations of the residual potential SiON₂ post-treatment compounds) after a thermal treatment beyond 900°C in a nitrogen ambient. --

Please replace the paragraph commencing at line 17, page 21, with a new paragraph as follows:

-- Figure ((9))8a shows the in-depth FTIR spectra from 1700 to 2200 cm⁻¹ of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. This region of interest focuses on the Si=O oscillators, centered at 1875

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cm⁻¹ of four (4) of the six (6) residual potential post-treatment compounds: SiO₂, SiOH₂, SiONH and SiON₂. Another unknown absorption peak is also observed centered at 2010 cm⁻¹ but since this unknown oscillator does not have a higher harmonics which could cause optical absorption in the 1.30 to 1.55 μm optical bands, the search of its identity was not prioritized. It is clear that the higher the thermal decomposition temperature of the high temperature thermal treatment from 600 to 1100°C in a nitrogen ambient, the more evident the Si=O oscillators (which fourth harmonics could cause an optical absorption between 1.282 and 1.389 μm) and the more evident the unknown oscillators which have no higher absorption harmonics between 1.300 and 1.550 μm. --

Please replace the paragraph commencing at line 3, page 22, with a new paragraph as follows:

-- Figure ((10a))9a shows the in-depth FTIR spectra from 2200 to 2400 cm⁻¹ of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. This region of interest focuses on the Si-H oscillators, centered at 2260 cm⁻¹ of three (3) of the six (6) residual potential post-treatment compounds: SiNH, SiOH₂, and SiONH. It is clear that the higher the thermal decomposition temperature of the high temperature thermal treatment in a nitrogen ambient, the better the elimination of Si-H oscillators (which third harmonics could cause an optical absorption between 1.443 and 1.508 μm) with a complete elimination of residual Si-H oscillators (i.e. some configurations of the residual potential SiNH, SiOH₂, and SiONH post-treatment compounds) after a thermal treatment beyond 600°C in a nitrogen ambient. --

Please replace the paragraph commencing at line 15, page 22, with a new paragraph as follows:

-- Figure ((11a))10a shows the in-depth FTIR spectra from 3200 to 3900 cm⁻¹ of typically deposited PECVD silica films before and after a three hours long high temperature thermal treatment in a nitrogen ambient at a temperature of either 600, 700, 800, 900, 1000 or 1100°C. This region of interest focuses on the Si:N-H oscillators, centered at 3380 cm⁻¹, the SiN-H oscillators, centered at 3420 cm⁻¹, the SiO-H oscillators, centered at 3510

cm⁻¹ and the HO-H oscillators, centered at 3650 cm⁻¹ of three (3) of the six (6) residual potential post-treatment compounds: SiNH, SiOH₂ and SiONH. It is clear that the higher the thermal decomposition temperature of the high temperature thermal treatment from 600 to 1100°C in a nitrogen ambient, the better the elimination of: --

Please replace the paragraph commencing at line 9, page 23, with a new paragraph as follows:

-- ~~The upper Figures ((6a))~~5a to Figure ((11a))10a show that it is very difficult to completely eliminate the residual oscillators of the various undesirable Si-O_x-H_y-N_z potential post-treatment compounds and achieve optical quality silica films from typically deposited PECVD silica films using thermal treatments at temperature between 600 and 1100°C in a dry (nitrogen) ambient. --

Please replace the paragraph commencing at line 3, page 24, with a new paragraph as follows:

-- Figure ((6b))5b shows the basic FTIR spectra of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. It is clear that the control of the deposition pressure of this improved PECVD deposition technique has a major effect on the FTIR spectra of the treated silica films (i.e. the better the four basic optical absorption peaks): --

Please replace the paragraph commencing at line 14, page 14, with a new paragraph as follows:

-- An in-depth examination of some infrared regions of the FTIR spectra of Figure ((6b))5b with the help of the FTIR regions of the table of Figure ((5))4 could help verifying the gradual elimination of the various Si-O_x-H_y-N_z potential as-deposited compounds and verify the gradual achievement of pure SiO₂ with minimum optical absorption in the 1.30 to 1.55 μm optical bands as the pressure is changed around this optimum deposition pressure of 2.40 Torr. --

Please replace the paragraph commencing at line 9, page 25, with a new paragraph as follows:

-- Figure ((7b))6b shows the in-depth FTIR spectra from 810 to 1000 cm⁻¹ of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. This region of the FTIR spectra should show a net separation between the Si-O-Si "in-phase-stretching mode" absorption peak (1080 cm⁻¹) and the Si-O-Si "bending mode" absorption peak (810 cm⁻¹) and should show a deep valley between 850 and 1000 cm⁻¹. It is clearly observed that there is a gradual elimination of the residual Si-OH oscillators (centered at 885 cm⁻¹) of the residual SiOH₂ residual post-treatment compound (Figure 4) as the deposition pressure is increased from 2.00 Torr up to the optimum pressure of 2.40 Torr and that the elimination gradually get worse as the pressure is further increased from the optimum 2.40 Torr up to 2.60 Torr. Similarly, it is clearly observed that there is a gradual elimination of the Si-ON oscillators (centered at 950 cm⁻¹) of the residual SiONH and/or SiON₂ post-treatment compounds (Figure 4) as the deposition pressure is increased from 2.00 Torr up to the optimum 2.40 Torr and then gradually less effective as the deposition pressure is further increased from this optimum 2.40 Torr up to 2.60 Torr. The optimum separation and deep valley observed at 2.40 Torr is an indication that the silica films resulting from this optimum deposition pressure are composed of high quality SiO₂ material. --

Please replace the paragraph commencing at line 1, page 26, with a new paragraph as follows:

-- Figure ((8b))7b shows the in-depth FTIR spectra from 1500 to 1600 cm⁻¹ of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. This region focuses on the N=N oscillators (centered at 1555 cm⁻¹ and which fifth harmonics could cause an optical absorption between 1.266 and 1.307 μm) of the various residual post-treatment compounds of Figure 4. It is observed that these oscillators are gradually eliminated as the deposition pressure is increased from 2.00 up to the

optimum pressure of 2.40 Torr and that the elimination is gradually (slight effect) less complete as the pressure is further increased from this optimum pressure of 2.40 up to 2.60 Torr. --

Please replace the paragraph commencing at line 11, page 26, with a new paragraph as follows:

-- Figure ((9b))8b shows the in-depth FTIR spectra from 1700 to 2200 cm⁻¹ of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. This region focuses on the Si=O oscillators (centered at 1875 cm⁻¹) and on the unknown oscillator (centered at 2010 cm⁻¹) of the various residual post-treatment compounds described by Figure 4. It seems that even at the optimum deposition pressure of 2.40 Torr, it is not possible to eliminate the Si=O oscillators (which fourth harmonics could cause an optical absorption between 1.282 and 1.389 μm) and the unknown oscillators (which does not have a higher harmonics which could cause optical absorption in the 1.30 to 1.55 μm optical bands) at any of the deposition pressures. This limitation is not that important since only the fourth harmonics of the Si=O oscillators which can absorb in the 1.30 to 1.55 μm optical bands. --

Please replace the paragraph commencing at line 24, page 26, with a new paragraph as follows:

-- Figure ((10b))9b shows the in-depth FTIR spectra from 2200 to 2400 cm⁻¹ of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. This region focuses on the Si-H oscillators (centered at 2260 cm⁻¹) of the various residual post-treatment compounds of Figure 4. It is clear that the Si-H oscillators (which third harmonics could cause an optical absorption between 1.443 and 1.508 μm) are completely eliminated for all deposition pressures. --

Please replace the paragraph commencing at line 3, page 27, with a new paragraph as follows:

-- Figure ((11b))10b shows the in-depth FTIR spectra from 3200 to 3900 cm⁻¹ of silica films obtained with the improved PECVD deposition technique after a three hours long high temperature thermal treatment in a nitrogen ambient at a low temperature of 800°C. This region focuses on the Si:N-H oscillators (centered at 3380 cm⁻¹), on the SiN-H oscillators (centered at 3420 cm⁻¹), on the SiO-H oscillators (centered at 3510 cm⁻¹) and on the HO-H oscillators (centered at 3650 cm⁻¹) of the various residual post-treatment compounds described by listed in Figure ((4))3. It is clear that all these oscillators are gradually eliminated as the deposition pressure is increased from 2.00 to 2.60 Torr. --

Please replace the paragraph commencing at line 6, page 28, with a new paragraph as follows:

-- A systematic comparison between: (Figures ((5a))4a and ((5b))4b), (Figures ((6a))5a and ((6b))5b), (Figures ((7a))6a and ((7b))6b), (Figures ((8a))7a and ((8b))7b), (Figures ((9a))8a and ((9b))8b) as well as (Figures ((10a))9a and ((10b))9b) shows the spectacular benefits of the improved PECVD deposition technique which results in a substantially total elimination of the various undesirable Si-O_x-H_y-N_z potential post-treatment compounds after a low temperature (800°C) thermal treatment in a nitrogen ambient and in particular of the residual SiONH post-treatment compounds which can still be detected by the residual Si:N-H oscillators (centered at 3380 cm⁻¹ and which second harmonics causes an optical absorption between 1.445 and 1.515 μm) of ~~Figure 11a's the~~ 1100°C curve shown in Figure 10a. By contrast, it is clear that these residual Si:N-H oscillators are completely eliminated from ~~Figure 11b's the~~ 2.40 Torr curve of Figure 10b, even after a much lower temperature (800°C) thermal treatment in the same nitrogen ambient. --

Please replace the paragraph commencing at line 27, page 28, with a new paragraph as follows:

-- The comparison of the various PECVD approaches summarised in Figure-Table 1 shows that the novel PECVD approach has a number of advantages: it does not require the use of B and/or P; it does not use TEOS; it does not use O₂; it does not use CF₄; it does not use SiH₄, N₂O and NH₃ gas mixtures; it does not use SiH₄, N₂O and Ar gas

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mixtures; it does use more than just SiH₄ and N₂O gas mixtures; and while it does use SiH₄, N₂O and N₂ gas mixtures, it does so in a very different way from the cited prior art (Imoto K., 1993) which only reports the control of the mass flow rates of the three gases as a way to control the transparency and refractive index of the silica film. --

Please replace the paragraph commencing at line 7, page 29, with a new paragraph as follows:

-- The described technique uses an independent control of the SiH₄, N₂O and N₂ gases as well as of the total deposition pressure via an automatic control of the pumping speed of the vacuum pump. As mentioned before the fundamental principles of classical thermodynamics predict that the equilibrium constants of the various chemical reactions of Figure ((3))2 will be affected by the total deposition pressure and will result in an improved elimination of some of thirty-five (35) Si-O_x-H_y-N_z potential as-deposited compounds due to an improved elimination of N₂, O₂, HNO, NH₃, H₂O, and H₂ gaseous compounds that must be eliminated from the micro-pores of the growing silica films up to their surface and from their surface through the gaseous boundary layer present near their surface. This effect is due to the fact that many of the chemical reactions of Figure ((3))2 are associated with a modification of the number of gaseous compounds; i.e. the number of gaseous product compound molecules is different than three, the number of gaseous reactant compound molecules:



Please replace the paragraph commencing at line 8, page 30, with a new paragraph as follows:

-- The spectacular effect of the total deposition pressure was demonstrated by the FTIR spectra of: Figure ((5b))4b, Figure ((6b))5b, Figure ((7b))6b, Figure ((8b))7b, Figure ((9b))8b and Figure ((10b))9b which compare the results of silica films deposited at the following fixed gas flows: --

Please replace the paragraph commencing at line 26, page 30, with a new paragraph as follows:

-- The spectacular effect of this fourth independent variable, the total deposition pressure, on the elimination of the various undesirable Si-O_x-H_y-N_z potential post-treatment compounds after a low temperature (800°C) thermal treatment in a nitrogen ambient is clearly demonstrated by comparing: (Figures ((5a))4a and ((5b))4b), (Figures ((6a))5a and ((6b))5b), (Figures ((7a))6a and ((7b))6b), (Figures ((8a))7a and ((8b))7b), (Figures ((9a))8a and ((9b))8b) as well as (Figures ((10a))9a and ((10b))9b). In particular, it is demonstrated that the residual Si:N-H oscillators of the residual SiONH post-treatment compounds (centered at 3380 cm⁻¹ and which second harmonics causes an optical absorption between 1.445 and 1.515 μm) are completely eliminated from ~~Figure 11b~~^sthe 2.60 Torr curve of Figure 10b even after a low temperature thermal treatment of only 800°C in nitrogen. This contrasts with the results of Figure ((11a))10a which shows that a much higher temperature thermal treatment of 1100°C in nitrogen is required to eliminate the same oscillators from silica films obtained from typical non-optimized PECVD conditions.--

Please replace the paragraph commencing at line 13, page 31, with a new paragraph as follows:

-- Figure ((12))11 summarises the spectacular effect of this fourth independent variable, the total deposition pressure, on the integrated area under the 3380 cm⁻¹ FTIR peak of the Si:N-H oscillators of PECVD silica films deposited at a fixed SiH₄ gas flow of 0.20 std liter/min, at a fixed N₂O gas flow of 6.00 std liter/min and at a fixed N₂ gas flow of 3.15 std liter/min and following a thermal treatment in a nitrogen ambient at 800°C.--

Please replace the paragraph commencing at line 19, page 31, with a new paragraph as follows:

-- The elimination of the residual Si:N-H oscillators at lower temperature is not the only benefit of the technique described according to the invention. Figure ((13))12 shows the effect of the total deposition pressure on the 1.55 μm refractive index of PECVD silica films deposited at a fixed SiH₄ gas flow of 0.20 std liter/min, at a fixed N₂O gas flow of 6.00 std liter/min and at a fixed N₂ gas flow of 3.15 std liter/min and following a

thermal treatment in a nitrogen ambient at 800°C. It is again clear that the introduction of the fourth independent variable, the total deposition pressure, is critical for the development of optimized optical silica films. The refractive index at the operation wavelength of 1.55 μm is certainly one of the most important film characteristic. This Figure ((13))12 clearly indicates that the control of this parameter is of prime importance for the repeatable achievement of high quality optical silica films. At this point it should be noted that typical vacuum pumping systems used in PECVD equipment (i.e. rotary vane mechanical pumps, roots blowers, turbo-molecular pumps or others) suffer from many sources of pumping speed variation over time (variation of the AC electrical power source, variation of the pumping conductance due to accumulation of residues in the protection scrubber or pumping lines etc) and it is then expected that a PECVD deposition condition involving a fixed set of gas flow parameters will suffer from a non-repeatability of the observed film characteristics. --

Please replace the paragraph commencing at line 9, page 32, with a new paragraph as follows:

-- Figure ((14))13 summarises the effect of the N₂O mass flow rate on the integrated area under the 3380 cm⁻¹ FTIR peak of the Si:N-H oscillators of PECVD silica films deposited at a fixed SiH₄ gas flow of 0.20 std liter/min, at a fixed N₂ gas flow of 3.15 std liter/min, at a fixed total deposition pressure of 2.60 Torr and following a thermal treatment in a nitrogen ambient at 800°C. It is very clear that once the local optimum operation point is found in the five dimensional space (four independent variables and one output measurement), there might be no further relationship between the residual optical absorption of the obtained silica films and that the SiH₄-to-N₂O gas flow ratio is actually not a determining factor. Again, since the optical transparency at the operation wavelength of 1.55 μm is certainly one of the most important film characteristic of optical silica waveguides, this Figure ((14))13 clearly indicates that, unlike for what is reported in the previous art literature, the SiH₄-to-N₂O gas flow ratio is not an important factor in the definition of the optical properties of silica films. --

Please replace the paragraph commencing at line 23, page 32 with a new paragraph as follows:

-- Figure ((15))14 shows the effect of the N₂O gas flow on the 1.55 μm refractive index of PECVD silica films deposited at a fixed SiH₄ gas flow of 0.20 std liter/min, at a fixed N₂ gas flow of 3.15 std liter/min, at a fixed total deposition pressure of 2.60 Torr and following a thermal treatment in a nitrogen ambient at 800°C. It is again very clear that once the local optimum operation point is found in the five dimensions space (four independent variables and one output measurement), there might be no more relationship between the measured film characteristics and the ratio of SiH₄-to-N₂O gas flow ratio. Again, since the refractive index at the operation wavelength of 1.55 μm is certainly one of the most important film characteristic of optical silica waveguides, this Figure ((15))14 clearly indicates that the SiH₄-to-N₂O gas flow ratio is not a critical factor in the definition of the optical properties of silica films.

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